Electrolytes in the presence of a potential barrier: Diffusio-osmotic flow

Author: Sergio Granados Leyva.
Facultat de Física, Universitat de Barcelona, Diagonal 645, 08028 Barcelona, Spain.

Advisor: Ignacio Pagonabarraga

Abstract: In this paper, we study the influence of a potential barrier in a symmetric electrolyte fluid embedded on a parallel plate. A generalisation of the Gouy-Chapman model is derived in the presence of this barrier and analytical solutions are obtained for the linearised regime and the electroosmotic flow for small barriers. The expressions are complemented with Lattice-Boltzmann simulations, determining the region where the linearisation works and extending the validity of the linearised regime when the height of the barrier increases. Finally the electroosmotic velocity profiles are analytically reproduced using the modified linearisation and compared to the simulations.

I. INTRODUCTION

The main motivation for this article is to understand and characterise the behaviour of diffusio-osmotic flows using macroscopical parameters. To simulate these flows a potential barrier can be defined at the solid boundary, say x-y plane and z=0, accounting the interaction between the solid boundary and the solute. The barrier would act only on the solute and would set a characteristic concentration profile. If now, a constant uniform chemical potential gradient is set in the x direction far from the boundary, at $z \equiv \infty$, a velocity profile associated to a diffusio-osmotic flow is developed. In references [1] and [2] from where we have taken the inspiration for this work a mechanical approach to the problem is given analytically and then compared to simulations results using a molecular dynamics method. They use the concept of osmotic pressure and the concentration profiles to obtain the velocity profile and the diffusio-osmotic mobility coefficient. As there is no existence of a simulation method that allows to introduce a chemical potential gradient compatible with periodic boundary conditions they impose a constant force to each solute particle and compare to the derived expressions. This can be done, for example, using a ionic solute and a constant electric field. Understanding such behaviours and being able to manipulate such regimes would result in an incredibly efficient control of solute transport and would allow to improve microfluidic devices and develop new ones in a world that works at a smaller scale every day. What we do in this article is to study a similar situation using typical fluid parameters. To compare the results we use a professional code called Ludwig.

Ludwig is an open source code that uses a discretised version of the Boltzmann kinetic equation. This kind of mesoscopic simulation models are called Lattice-Boltzmann (LB) models, as space and velocities are discretised in a number of nodes forming a lattice. The details and the development of the method can be found in references [3] and [4]. The context of this methodology of simulation will be briefly exposed in this section.

To enlighten the advantages and the need of using a code like Ludwig another completely different simulation method can be compared. In molecular dynamics methods, for example, Newton's equation of motion is solved for a bunch of solute and solvent particles. In these methods interacting mass points are being simulated, instead of a discretised lattice in space. The solvent cannot be reduced to structureless points as the system would never reach thermal equilibrium. The most obvious disadvantage is not difficult to determine: Its computational cost. Also, there is an impossibility to somehow "turn off" isothermal fluctuations as they are an inner part of the approach. Another inconvenient is that there is no direct access to macroscopical parameters of the fluid such as viscosity and diffusivity. The LB method, on the other side, describes the solvent on a more simplified fashion that still can reproduce the hydrodynamic behaviour and the conservation laws. It uses the definition of a free energy as a function of an order parameter so that we can manipulate macroscopical variables. For example, viscosity, permittivity, temperature and diffusivity can be directly defined in the system which gives access to the study of the behaviour of the fluid as a function of these parameters in macroscopical expressions as Navier-Stokes and Poisson equations.

We will use Ludwig to do a first approach to a problem similar to diffusio-osmotic flow based in macroscopical equations. The size of the system will be small so that gravity can be neglected and the regime is a surface driven flow. We will study the influence of the presence of a potential barrier in a electrolyte embedded in a parallel plate. The barrier will be placed at the center of the system, and not in the solid boundary to obtain symmetric solutions. Ludwig parameters allows to study the problem using a modified Gouy-Chapman model, as the concentration ions will follow a similar profile to that characterised by the Debye length near the potential barrier. The introduction of the potential barrier affects drastically and limits the linearised regime, called Debye-Huckel approximation, which allows to obtain analytical expressions and study the problem quantitatively. It will be seen how to extend the model in this region so that the studied cases are not limited to almost flat potential profiles.

II. A REMINDER: THE GOUY-CHAPMAN MODEL

Suppose an electroneutral charged fluid in contact with a solid boundary wall. The valency of the species will be +Z and -Z, being a symmetric fluid electrolyte. We denote by x the axis perpendicular to the surface wall, and y, z the other components. If this plate now is positively charged, negative ions will be more likely to be near the wall. This argument work backwards for positive ions. It can be shown using statistical mechanics and thermodynamics that the chemical potential of each solute specie, corresponding to +Z and - Z, is

$$\mu_{\pm}(\vec{r}) = \mu_0 + k_B T \ln\left(\frac{\rho_{\pm}(\vec{r})}{\rho_0}\right) \pm Zq\phi(\vec{r}) \qquad (1)$$

Imposing that the chemical gradient is 0 at equilibrium, the expression for the bulk charge density of each specie can be derived knowing that the difference between the species is proportional to the electric density at each point of the space. This electric density can be plugged in Poisson equation to determine the potential profile. The differential equation to solve, at the end is

$$\nabla^2\phi(\vec{r}) = 2\frac{Ze\rho_0}{\varepsilon}\sinh\left(\frac{Ze}{k_B T}\phi(\vec{r})\right)$$

which can be analytically solved considering only the x coordinate, as the problem is symmetric respect y and z. If the thermal energy $k_B T$ is much greater than the potential, equation (3) can be reduced, using Taylor expansion to an even simpler differential equation, the solution of which is

$$\phi = \phi_w \exp\left(-\frac{x}{\lambda_D}\right)$$

This is the Debye-Huckel approximation. The negative ions will shield the positive charged wall within a characteristic length, called Debye length λ_D, which naturally arises in solving the problem and is defined as

$$\lambda_D = \sqrt{\frac{\varepsilon k_B T}{2(Ze)^2\rho_0}} \qquad (2)$$

This approach is called the Gouy-Chapman model. If now another charged plate parallel to the first one and placed in a distance L_x is considered, and an external, constant, not very intense electric field perpendicular to the x axis is applied, the fluid will move following the Navier-Stokes equation at low Reynolds number

$$-\nabla P + \eta\nabla^2\vec{v} - \rho_{el}^{eq}\nabla\phi_{ext} = 0 \qquad (3)$$

The pressure gradient is 0 if no force other than electric field acts on the fluid. The charge q is proportional to the difference of density species which at the same time follows the Poisson equation. For the latter reason the velocity profile will follow $v_y(x) \propto \phi$. This corresponds to an electroosmotic flow. Both Gouy-Chapman model and electroosmotic flow problems can be found solved in references [5] and [6].

III. POTENTIAL BARRIER: ANALYTICAL EXPRESSIONS

In the case of introducing a potential barrier, the latter expressions have to be modified. The system considered, in the following derivations and simulations will be a slit pore of length L_x. The extension of the other lengths will be considered infinite to obtain symmetric solutions to the problem. The introduced potential barrier will be a Gaussian function

$$U(x) = Ae^{-\frac{(x-x_0)^2}{\sigma^2}} \qquad (4)$$

where A is a constant that characterises the height of the barrier. The factor σ characterises the thickness of this barrier and x_0 centers the barrier around it's value. In the following derivations the barrier will be placed at the center of the system.

The system is, again, a fluid that has two electric species with valencies +Z and -Z. There are several options in introducing the potential barrier that will lead to different solutions, some of them more interesting than others. Imagine now for simplicity that there is no wall surface charge. The potential barrier could be introduced, for example, for both species. This would make both ion species to move off from the barrier following the same density profile. In this case, the fluid would be locally electroneutral: The potential profile would be constant all along the system. There wouldn't be any response in applying an electric field. Now imagine that we are somehow able to impose the barrier just to one of the species, say +Z: At equilibrium we can guess that, as the positive ions feels a force due to this potential barrier, this ions are going to move off the centre of the barrier. Negative ions does not feel any force directly provided by the barrier, but as there is an accumulation of positive charge, negative ions are going to feel an attractive force coming from this accumulation. To sum up: negative ions will be, as positive ions, less likely to be inside the barrier as a consequence of the attraction felt by the positive ions accumulation. This time the system is not going to be locally electroneutral. It will have a characteristic potential profile and will response in application of an external electric field. The solutions will be now briefly characterised for this potential and density profiles.

Physically, this barrier can be theoretically introduced as an extra term in the chemical potential, as the energetic cost of adding ions is being incremented where the barrier is placed. This will reconfigure the equilibrium distribution of concentration and the total potential. With the system conditions given at the beginning of this section, the problem will eventually become a 1-D problem. As a first step, the chemical potential expression with this extra barrier term will be considered. It can't be assumed this time that the constant dividing the density function, ρ_0, is the same for both species and is constant far from the walls as in GP model. In general far from the walls the densities will have different values depending on the height of the barrier so that a different

constant to each specie have to be assigned, related to the charge at the surface, ρ_-^0 and ρ_+^0. Now, equation (1) will be:

$$\mu_\pm(\vec{r}) = \mu_0 + k_B T \ln\left(\frac{\rho_\pm(\vec{r})}{\rho_\pm^0}\right) \pm Zq\phi(\vec{r}) + A_\pm e^{-\frac{(x-x_0)^2}{\sigma^2}}$$

In the thermodynamic equilibrium, the gradient of this chemical potential must be 0. Imposing this in the latter equation, the boundary conditions defining a potential far from the wall $\phi(\infty) = \phi_0$ can be set, obtaining the expression for each density specie

$$\rho_\pm(\vec{r}) = \rho_\pm^0 \exp\left(\frac{\mp Zq\phi(\vec{r}) - A_\pm e^{-\frac{(x-x_0)^2}{\sigma^2}}}{k_B T}\right) \quad (5)$$

Setting $A_+ = A$ and $A_- = 0$ the electric density can be determined

$$\rho_{el}(\vec{r}) = \rho_+^0 Zq \exp\left(\frac{-Zq\phi(\vec{r}) - Ae^{-\frac{(x-x_0)^2}{\sigma^2}}}{k_B T}\right) - \rho_-^0 Zq \exp\left(\frac{+Zq\phi(\vec{r})}{k_B T}\right)$$

which in the Debbye-Huckel approximation allows a linearisation of the form

$$\rho_{el}(\vec{r}) = \frac{Zq}{k_B T}\left(-\phi(\vec{r})\rho_t^0 - \rho_+^0 Ae^{-\frac{(x-x_0)^2}{\sigma^2}} + \Delta\rho^0\right) \quad (6)$$

where $\Delta\rho^0 \equiv \rho_+^0 - \rho_-^0$ and $\rho_t^0 \equiv \rho_+^0 + \rho_-^0$. The Debye-Huckel approximation additionally implies that the height of the barrier cannot have an arbitrary large value as the linearisation would break down. Introducing this electric density in the Poisson equation will lead to

$$\phi'' - B\phi = A' e^{-\frac{(x-x_0)^2}{\sigma^2}} - \frac{Zq\Delta\rho^0}{\varepsilon} \quad (7)$$

where B=$Zq\rho_t^0/\varepsilon k_B T$, and $A' = \rho_+^0 AZq/\varepsilon k_B T$. This is a non-homogeneous second order linear differential equation. It can be solved using the varying constant method described in detail in reference [7]. The solution is not entirely analytical but can be written in terms of the error function. The procedure is large and delicate, so that here is only shown the obtained solution:

$$\phi(x) = c_1 e^{\sqrt{B}x} + c_2 e^{-\sqrt{B}x} + b_1(x) + b_2(x) - \frac{Zq\Delta\rho^0}{\varepsilon} \quad (8)$$

$$b_1(x) = K_1 \cdot \mathrm{erf}\left(\frac{\sqrt{B}\sigma^2 - 2x_0 + 2x}{2\sigma}\right) e^{\sqrt{B}x}$$

$$K_1 = \frac{A\sigma\sqrt{\pi}}{4\sqrt{B}} e^{\frac{\sqrt{B}}{4}(\sqrt{B}\sigma^2 - 4x_0)}$$

$$b_2(x) = K_2 \cdot \mathrm{erf}\left(\frac{\sqrt{B}\sigma^2 + 2x_0 - 2x}{2\sigma}\right) e^{-\sqrt{B}x}$$

$$K_2 = \frac{A\sigma\sqrt{\pi}}{4\sqrt{B}} e^{\frac{\sqrt{B}}{4}(\sqrt{B}\sigma^2 + 4x_0)}$$

The coefficients c_1 and c_2 are determined via boundary conditions. Placing the barrier at the centre of the system the first boundary condition is imposed by the symmetry of the seek solution: The potential at both plates have to be the same, $\phi(0) = \phi(L_x)$. The other boundary condition is the potential at the surface, $\phi(0) = \phi_s$. This potential is not merely an origin, as it has already been fixed in equation (5) and it has a determining effect in the shape of the solution. In the following solutions this parameter will be set in a way that the derivative of the potential at the walls is 0 so there is no charge associated.

In the case of applying an electric field to simulate the diffusio-osmotic flow, the velocity profile follows the shape of the equilibrium potential as stated in previous section. In particular, equation (3), setting an electric field $\vec{E} = E_x \vec{j}$ and considering that in equilibrium there is a velocity profile of the form $v_y(x)$ the relation between the electric density and the potential leads to

$$\frac{\partial^2}{\partial x^2}\left(v_y(x) - \frac{E_x}{\eta}\right) = 0$$

and can be easily solved using the boundary conditions $v_y(0) = v_y(L_x) = 0$ to obtain

$$v_y(x) = \left(\frac{\phi_{eq}(x)}{\phi_s} - 1\right)\frac{\varepsilon\phi_s}{\eta} E_x \quad (9)$$

The factor proportional to the electric field arises in several electroosmotic phenomena and is called electroosmotic mobility. Is defined as

$$\frac{\phi_s \varepsilon}{\eta} \equiv \mu_{eo}$$

and characterises the response to an external, constant electric field.

IV. LUDWIG SIMULATIONS

In the simulations some parameters will be fixed to focus on the relation between the height of the barrier and the ionic reorganisation. These parameters will be the viscosity of the solvent $\eta = 0.1$, the initial uniform bulk charge density $\rho_0 = 0.001$, the diffusivities for each specie $D_0 = 0.01$ and $D_1 = 0.01$, the valencies for each specie $Z_0 = 1$ and $Z_1 = -1$, the permittivity $\varepsilon = 3300$, the unit charge e=1, the barrier thickness $\sigma = 4$ and the Boltzmann thermal energy $k_B T = 3.3333 \cdot 10^{-5}$. The system will be a L_xx4x4 box. There won't be any charge at the walls. Periodic conditions ensures that the system is equivalent to an infinite one in both y and z axis. The introduction of the barrier cannot be directly done in the Ludwig input file as it is not naturally defined and we had to modify the subroutines of the code. This was a non trivial issue which required several months of investigation.

Once these parameters are fixed, depending on the height of the barrier we can encounter three more or less differentiated regions.

1. A region where the height is small so that the linearisation works and the simulation potential and density profiles coincide with the analytical expressions. This happens if $|-\phi(x_c)-A| \ll k_BT$, where x_c is defined as the centre of the system.

2. A region where $|\phi(x_c)| < k_BT$ but $A \simeq k_BT$: The linearisation will be broken only near the centre of the system where the barrier takes the maximum value.

3. A region where $|-\phi(x_c)-A| \gg k_BT$ where the linearisation will be totally broken.

Some simulations were performed and the obtained potential profiles compared to the analytical ones in equation (8). In Fig 1 some of this comparisons are shown. It is seen that initially the approximation fits the curve but eventually overestimates the potential at the centre. It is seen also that the analytical height of the profile with A=0.6 seems to fit better the simulation profile at A=0.9 than its corresponding analytical profile. This overestimation increases with A. Representing the bulk charge density it is observed an overestimation of positive ions near the wall and an underestimation of negative ions at the centre.

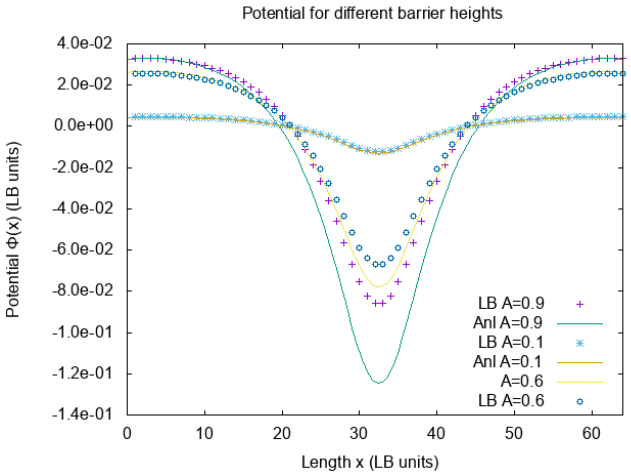

FIG. 1: Potential profiles for different barrier heights. Here LB refers to Lattice-Boltzmann obtained profiles and "anl" to analytical profiles corresponding to the given expression

To study the way in which the linearisation breaks more simulations were performed. It was studied how the difference between the analytical profile and the simulation profile increased with A. The results are shown in Fig 2. The error initially increases slowly but eventually grows at a bigger slope. The region where the increase is slower admits a satisfying correction of the linearisation. This correction is made multiplying the barrier height in equation (8) for a constant $0 < \xi < 1$ that reduces the overestimation made at the centre of the barrier. It acts as some kind of effective potential height. In the expression of the density species, however, the original height must be used, as only the mathematical solution of the potential needs to be modified. In Fig 2 the correction factor is represented as a function of the barrier height. It is easy to distinguish the two latter enumerated regions separated by a small jump. The small jump is a consequence of entering the third region as the potential breaks the linearisation and the overestimation is compensated. Although the correction can be made in the third region the potential never fits the center. The correction is found to reproduce the simulated profile till an approximated value of the barrier of A $\simeq$ 2.4. Once the correction is introduced in the potential, the density species automatically fits the simulated profiles. In Fig 3 a particular case where this correction has been applied can be seen.

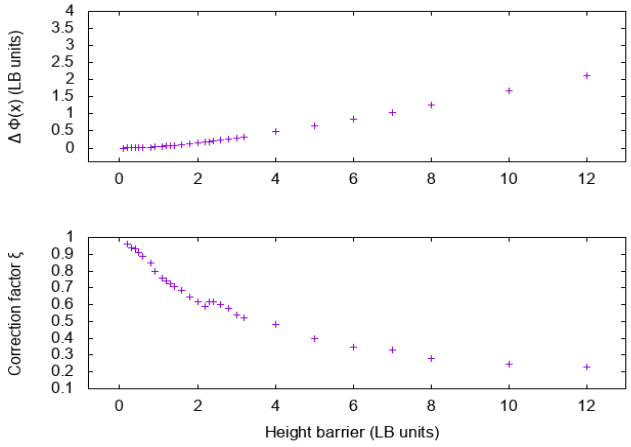

FIG. 2: Difference between analytical potential and simulation potential at the centre (above) and evolution of the correction factor (below), both as a function of the barrier height.

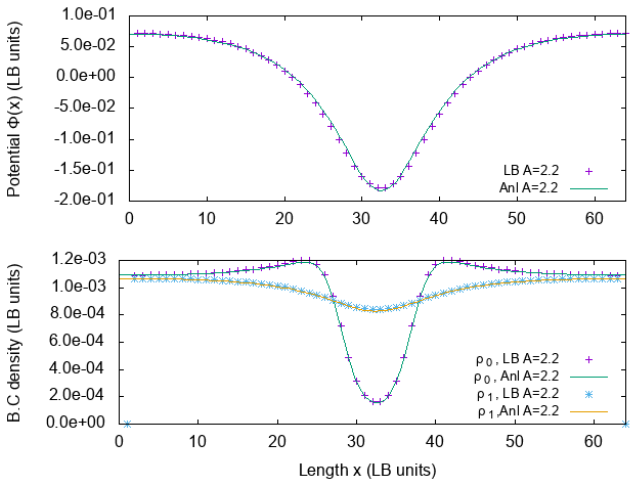

FIG. 3: Corrected potential and bulk charge density profiles. L_x has been fixed to 64.

Using the corrected equilibrium profiles, a constant electric field parallel to the y direction can be applied to characterise it's response using equation (9). The obtained results are shown in Fig 4 for a barrier of height A=0.9. The linear response of the fluid to the presence of the external electric field is observed and it is seen that equation (9) predicts perfectly the velocity profile.

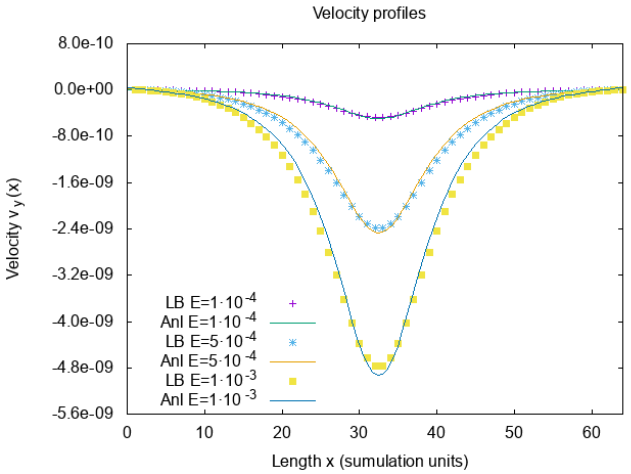

FIG. 4: Velocity profiles for different electric fields. Here, A is the same for all the profiles A=0.9 L_x has been fixed to 64. The electric field E is applied in the positive y direction.

V. CONCLUSIONS

In this article we have been able to characterise the important parameters dominating the behaviour of a complex fluid system where several different phenomenas compete with each other. A generalisation of the Gouy-Chapman model is derived in the presence of a potential barrier and some of the physical parameters of the problem are reinterpreted. In parallel, we have implemented a potential barrier in Ludwig LB method and validated the obtained solutions using simulations. A correction to the Debye-Huckel approximation is made and later predicted to extend the linearisation and reproduce correct results when the regime breaks down thanks to comparisons between simulations and analytical profiles. Whit this tools and characterisations, a new interesting velocity field profile is presented and studied. It presents a maximum value at the centre and a fast decrease towards zero velocity, due to the competition of electric forces caused by the ionic distribution and shear viscous forces. Although in these cases there have not been any charged walls, this can be easily implemented changing the boundary conditions of the mathematical solution and the validity of the correction holds. Other interesting velocity fields profiles can be observed in these charged wall cases.

The described regime still differs from the diffusio-osmotic flow studied in articles [1] and [2] but comprehension of this simplified model must not be underestimated. We have used a completely different approach to the problem, first obtaining the potential of the system and then the bulk charge density and predicting the velocity profile using well defined fluid parameters. The methodology developed here allows a more approachable framework to development of microfluidic devices in laboratories. Now that we understand the fundamental aspects of the problem, this model could be extended to more interesting regimes as potential barriers placed at both walls or near them. Having obtained solutions for this simpler problem a solid background is provided to compare and decide whether if forward modifications of the model still account the fundamental interactions between the fluid ions and the potential barrier or a more complex framework should be developed for the study of such situations.

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